

Defects Induced in Fused Silica by High Power UV Laser Pulses at 355 nm

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Abstract. Point defects induced in high quality optical-grade fused silica by high power (>30 J/cm²) 355 nm laser pulses have been investigated to elucidate the nature of laser damage in transparent optics designed for use at the National Ignition Facility (NIF). Six defects have been identified: the NBOHC (non-bridging oxygen hole center), a STE (self-trapped exciton), an ODC (oxygen-deficient center), interstitial oxygen, the E'_γ, and E'₇₄. The former four defects were identified and spatially resolved in the damage craters using cathodoluminescence (CL) microanalysis (spectroscopy and microscopy). The latter two defects were identified using ESR spectroscopy at cryogenic temperatures. These defects are unlikely to be a prime factor in damage growth by subsequent laser pulses. Their concentration is too low to effect a high enough temperature rise by a volume absorption mechanism.

With the advent of the National Ignition Facility (NIF) [1], now under construction at Lawrence Livermore National Laboratory, Livermore, California [2], and recent industrial interest in far UV lithography for microelectronics and telecommunication [3], laser-induced damage in transparent optics under high power UV irradiation has aroused considerable basic and technological interest in recent years [4]. A surge of multi-disciplinary approaches have been applied not only to elucidate the nature of laser-material interaction leading to damage, but also to provide technically viable and cost effective solutions for prolonging the lifetime of optical components.

Because of its optical properties in the UV region, high quality fused silica (SiO₂) is the material of choice for transmitting UV laser light (355nm or 3ω) to the target in the NIF laser system. The SiO₂-based optics include the focus lens, diffractive optic plates and the debris shield. Combined with the KDP (potassium dihydrogen phosphate) crystals used for frequency conversion of a Nd:glass laser (at 1.06 μm, 1ω), these optics make up the NIF final optic assembly [5].

Obscuration loss resulting from laser-induced damage on optical surfaces largely determines the operational lifetime of SiO₂ components on the NIF system. The obscuration arises from two processes: initiation of damage at an absorbing site at or near the surface, and damage growth upon subsequent irradiation [6,7]. Although progress has been made with studies

of polishing contaminations and subsurface damage to minimize the concentration of damage initiation sites on polished silica optics [8,9], the currently attainable defect densities of 1 per 100cm^2 would still render a non-acceptable number of damage sites on large optics such as the 40 cm x 40 cm lenses used on the NIF laser. A more direct approach is to perform detailed *archaeology* on the initiated damage sites by determining the material morphology and structural defects induced in fused silica with a view to aiding identification of the damage initiators and to elucidating the mechanism associated with the damage initiation process. This will help to establish a viable, knowledge-based methodology to mitigate or obviate damage growth.

This paper reports the determination of the point defects induced in fused silica by high fluence 3ω laser pulses using a combination of CL microanalysis [10] and high sensitivity ESR spectroscopy [11]. CL is the non-incandescent emission from a material irradiated with electrons. CL microanalysis in a scanning electron microscope (SEM) enables local variations in the defect structure to be characterized with high sensitivity and high spatial (lateral and depth) resolution [10]. This is the first determination of the microscopic distribution of defects in silica irradiated with high power 3ω laser pulses and gives insight into the fundamental processes associated with UV irradiation induced defect generation. The corresponding laser-induced morphology and microstructure in SiO_2 are reported elsewhere [12].

The starting fused silica (Corning 7940) substrates were 50mm diameter, x 10mm thick, and optically polished on both surfaces at commercial vendors. For CL measurements 10 mm cubes were cut prior to creation of the laser damage sites. For ESR measurements 2.27mm diameter rods were ultrasonically cored from the starting substrate. During cutting or coring the optical surfaces were protected with a solvent-removable paint. Laser damage sites were created using a 355 nm (3ω beam from a frequency tripled Spectra Physics GCR Nd-YAG laser. The pulse length (FWHM) was 7.5ns and the beam profile was near-Gaussian with an $1/e^2$ diameter of $\sim 0.9\text{mm}$ at the sample plane. The laser repetition rate was 10 Hz [13].

Damage sites were produced exclusively on the laser exit surface [14] using single or multiple pulses with fluences ranging from $30\text{--}45\text{ J/cm}^2$. Four damage sites were created at the corners of a 5mm square on each cube. For the rods, a pulse of 3ω light at 30 J/cm^2 was used to create a single damage site on the exit surface. After protectively covering the laser-damaged surface, a 1 mm thick end disk containing the laser-damaged crater was cut off using a diamond wire saw. Finally, any mechanically induced ESR-active centers (due to cutting and coring) were removed by etching ($\sim 60\text{ s}$) in aqueous HF (5% by volume).

Conventional cw ESR were carried out in the range 4.3-300 K using K-band ($\sim 20.5\text{ GHz}$) and Q-band ($\sim 33.5\text{ GHz}$) spectrometers under conditions of adiabatic slow passage. The amplitude of the modulation ($\sim 100\text{ KHz}$) of the applied magnetic field \mathbf{B} and incident microwave power P_μ were restricted to levels where no discernable signal distortion occurred. The latter was particularly pertinent for high-sensitivity low-T observations (requiring $P_\mu < 0.8\text{ nW}$ at 4.3 K in K-band). Generally, Q-band observations required intense signal averaging (500-1000 scans). Spin densities were determined by double numerical observation of the recorded dP_μ/dB spectra relative to a comounted calibrated isotropic Si:P spin standard recorded in one trace. The absolute accuracy reached is estimated at $< 20\%$, while the relative accuracy may be better than

10 %. The marker signal of $g_{\text{Si:P}}(4.3 \text{ K})=1.99869(2)$ also served as an accurate g reference. More details can be found elsewhere [11].

The CL apparatus and SEM have been described previously [10]. Electron beam power was minimized to reduce electron irradiation induced effects during data collection. The spectra are corrected for total instrument response. CL data from the laser damaged and undamaged fused silica surfaces are significantly different (Fig. 1). Prior to 3ω laser irradiation CL emissions are observed at 1.9 eV and 2.7 eV. Following laser irradiation, the emission intensities increase and in addition, low intensity emissions at 0.97 eV, 2.3 eV and 4.4 eV may also be observed (e.g. Fig. 1(d)). An increase in laser power and/or number of laser pulses enhances the CL emissions consistent with increases in the concentration of associated defects (see Fig. 1). The CL emissions can be identified with a variety of known fundamental defects generated by other energetic irradiations (e.g. electron, ion, x-ray, γ ray, etc [10,15-18] described below.

The 1.9eV emission is associated with the non-bridging oxygen hole center (NBOHC) and attributed to the recombination of electrons in the highly localized non-bridging oxygen band-gap state, with holes in the valence band edge [19]. The low intensity 2.3 eV emission is possibly associated with the radiative relaxation of the self trapped exciton (STE) which is a correlated electron-hole pair localized in a self-induced lattice distortion [20]. Luminescent emissions that are difficult to observe by photo-excitation such as the STE may be observed using CL techniques [21]. Localized thermal annealing of the molten core associated with the laser induced thermal explosion [12] reduces the concentration of competitive non-radiative defects, thereby enhancing the STE emission within the molten core. The 2.7eV and (very low intensity) 4.4eV emissions are attributed to transitions involving oxygen deficient defects (ODC) [15,16]. The 0.97eV emission has been identified as the singlet oxygen transition associated with interstitial neutral molecular oxygen (O_2) dissolved in the silica host lattice [22].

The microscopic spatial distribution of individual defects can be determined using monochromatic (i.e. energy selective) CL imaging. In Fig. 2. the (a) secondary electron image and (b) 2.7eV, (c) 1.9eV, and (d) 0.97eV monochromatic CL images from laser damaged silica are compared. The 2.7eV emission is spatially correlated with the molten core produced by thermal explosion. CL indicates the molten nodules and micro-fibers (not shown) resulting from the thermal explosion [23] are composed of strained oxygen deficient silica. The 1.9eV emission is more widely distributed and is correlated with the near concentric region of fractured material surrounding the molten core. Strained SiO_2 is a precursor of the NBOHC associated with the 1.9eV emission. Thus CL data is consistent with altered glass topology resulting from enhanced local strain in the vicinity of the laser damaged regions associated with mass loss (spallation) and/or densification (observed high concentration of oxygen deficient centers) due to laser generated shock waves and thermal explosion [12,23]. The 0.97eV emission associated with interstitial molecular oxygen is extremely weak, but clearly attenuated in the laser damaged region, and enhanced at the periphery (Fig.2(d)). The laser induced generation of ODCs results in the concomitant production of interstitial oxygen atoms which are desorbed or diffuse away from the molten core to the periphery of the damaged region during or as a result of the damage process. A proportion of the oxygen atoms have dimerized to form molecular oxygen at the periphery of the damage crater.

Fig. 3 shows a Q-band ($f = 33.47$ GHz) ESR spectrum of the ten 1-mm silica disks, each containing a damage site created by a pulse of 3ω light at 30 J/cm^2 . A central absorption feature having a zero-crossing g -value of 2.00053 ± 0.00004 , which is characteristic of the E'_γ center [15-17] is detected. The total concentration of E'_γ defects in the damaged silica disks was determined to be $(5 \pm 0.5) \times 10^{12}$, ie. $(5.0 \pm 0.5) \times 10^{11}$ defects/pulse on the average. In addition, a doublet at $g_c \sim 2.00125$ of splitting $73 \pm 1 \text{ G}$ was also present. Its intensity is $\sim 44 \pm 4\%$ of the central E'_γ signal, ie. $\sim 2.2 \times 10^{11}$ defects/pulse. This doublet has been studied in detail [24,25], and has been attributed to a hyperfine interaction arising from a H atom substituting one of the back oxygens bonding to the defective Si in the E' center (a H-associated E' -like center). This defect is commonly denoted as E'_{74} , or H(I) [17]. The source of the H comes from hydrogenic species present in the bulk silica, i.e., Corning 7940 contains 800-1000 wt ppm of OH [26]. Thus, from the total concentrations of E'_γ and E'_{74} determined herein, it appears that $\sim 44\%$ of all E' created by the 3ω laser irradiation have a backbonded H.

Given the above OH content in fused silica, the occurrence of the E'_{74} defects is perhaps not surprising. Yet, interestingly, the ratio $R = [E'_\gamma]/[E'_{74}] \sim 2.3$ would indicate that during the thermal explosion of crater formation, there is a much higher probability for E'_{74} creation than expected on grounds of atomic concentration. It is likely that during the explosive process, there is violent exchange of H, resulting in a relatively much enhanced E'_{74} density. It is therefore surprising [25] that no spur of the $E'_{10.7}$ doublet ascribed to $\text{HO}^\bullet\text{Si}=\text{O}_2$ is observed. An intense search has been carried out at low-T K band, but without success. Thus, within the precursor model $\text{O}_3\equiv\text{Si}-\text{Si}\equiv\text{HO}_2$ of the E'_{74} defect, it may indicate that during the thermal explosion [23], these strained Si-Si bonds, with H as part of the immediate structure, undergo a substantially higher probability for disruption.

The observed 3ω laser-induced defects in fused silica are summarized in Table 1 together with their known

TABLE 1. Observed 3ω laser-induced defects in fused SiO_2 : their optical and ESR properties

Defect	Proposed Structure	Optical spectra (eV) [17,20]	Half width(eV)	ESR[15-18]
NBOHC	$\equiv \text{Si} - \text{O}^\bullet$	Abs: 2.0 ($f = 4e^{-4}$) 4.8 ($f = 0.2$) CL, PL: 1.9 ($\tau = 10.2 \mu\text{s}$)	0.18 1.05 0.2	$g_c = 2.0095$
STE	?	Abs: 4.6 5.7 CL, PL: 2.3	0.4	
ODC	e.g. $\equiv \text{Si} : \dots (\text{Si} \equiv)$ $\rightarrow \sim 4.4 \text{ \AA} \leftarrow$	Abs: 3.15 ($f = 1.6e^{-7}$) 5 ($f = 0.15$) 6.9 ($f = 0.1-0.3$) CL, PL: 2.7 ($\tau = 10.2 \text{ ms}$), 4.4 ($\tau = 4.0 \text{ ns}$)	0.34 0.3 0.4 0.3 0.4	diamagnetic
O_2	O-O	Abs: 0.978 CL, PL 0.97	0.003	
E'_γ	$\equiv \text{Si}^\bullet \dots^+ (\text{Si} \equiv)$	Abs: 5.85 ($f = 0.14$) No CL and PL observed.	0.8	$g_c = 2.00053 \pm 0.00004$
E'_{74}	$= \text{HSi}^\bullet \dots^+ (\text{Si} \equiv)$	No CL and PL observed		$g_c = 2.00125 \pm 0.0001$

Notes: \equiv denotes Si bonding to 3 bridging oxygens in the silica glass structure; \bullet = an unpaired electron; Abs. = absorption; f = oscillator strength; CL = cathodoluminescence; PL = photoluminescence; τ = lifetime; $?$, the STE structure is controversial. Values in **bold** are determined in this study and equal to literature values; g_c is zero crossing g valu

optical and ESR properties. Monochromatic CL imaging indicates the absence of interstitial molecular oxygen (0.97 eV emission, Fig. 2(d)) and a concomitant high concentration of oxygen deficient defects (2.7 eV emission, Fig.2(b))

associated with the molten nodules in the core regions of the craters resulting from the thermal explosion [12,23]. Analysis of the depth profiles of these defects has also been performed using CL spectra collected as a function of electron beam energy, while keeping the beam power constant [27,28]. The results which will be reported in detail elsewhere [30], are consistent with damage initiation at the exit surface. Depth resolved CL microanalysis shows that the concentration of defects is greatest near the laser exit surface and monotonically decays to pre-irradiation levels at $\sim 10 \mu\text{m}$ depth below this surface.

From the geometry of the damage crater and the number of E'_γ centers created per pulse as determined from the ESR measurements, the concentration of this defect, N , induced in the damage crater to a depth of $10 \mu\text{m}$ is estimated to be $\sim 2.5 \times 10^{17}/\text{cm}^3$ (far below the maximum density ($\sim 5 \times 10^{19}/\text{cm}^3$ that may occur in bulk fused silica [30]). With this defect concentration, the known oscillator strength and spectral width given in Table 1, and using the Smakula's equation [31], an absorption coefficient, α , of $\sim 10 \text{ cm}^{-1}$ is estimated for the 5.85 eV absorption band of the E'_γ center. Assuming volume absorption, the temperature rise is given by $T = \alpha \cdot F / [\rho \cdot c_p]$, F is the laser fluence in J/cm^2 , ρ is the density of fused silica and c_p is the heat capacity. With $\alpha = 10 \text{ cm}^{-1}$, $F = 10 \text{ J}/\text{cm}^2$, $\rho = 2.2 \text{ gm}/\text{cm}^3$ and $c_p = 0.77 \text{ J}/\text{gm}/\text{K}$ for fused silica [26], a temperature rise of $\sim 60 \text{ K}$ is obtained. This estimate merely shows that the concentration of E'_γ defects created in the damage initiation process is too low to result in high enough energy absorption in a subsequent laser pulse to cause damage growth. It is, therefore, unlikely that volume absorption by induced defects, such as the E'_γ center and others listed in Table 1, are a prime factor for damage growth. Other mechanisms such as local E-field enhancement at cracks (Fig. 2a) and micro-pores [32], avalanche ionization, multi-photon absorption and other non-linear processes have to be considered [33, 34].

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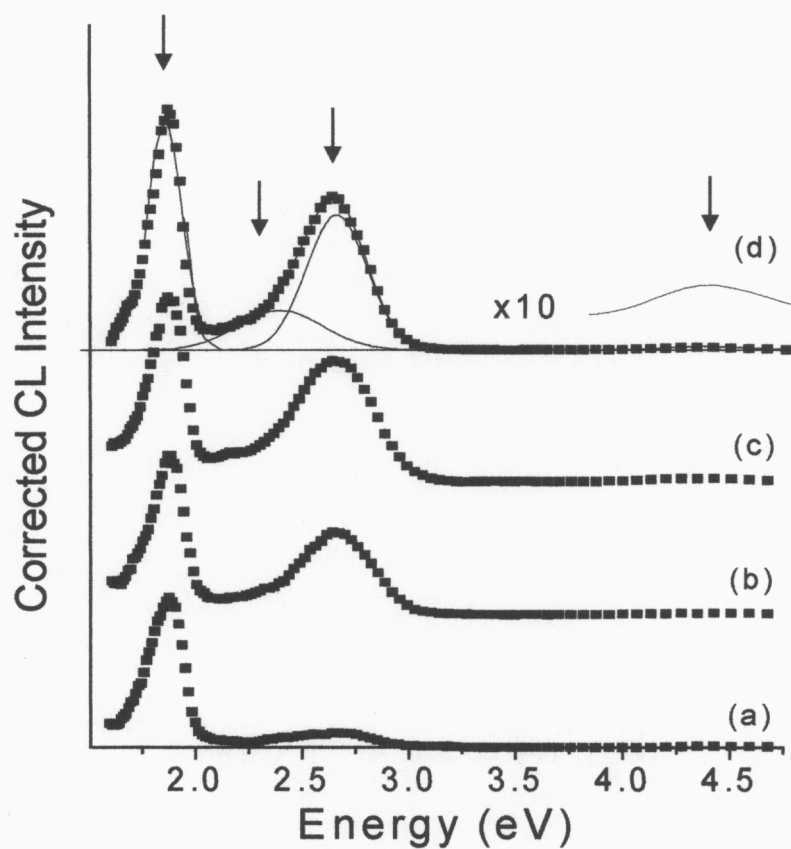


Fig. 1. Visible CL spectra (25keV, 1.5nA) from $150 \times 200 \mu\text{m}^2$ regions of fused silica: (a) undamaged area, and (b) 30 Jcm^{-2} , 1 pulse, (c) 30 Jcm^{-2} , 2 pulses and (d) 45 Jcm^{-2} , 1 pulse. Gaussian components are arrowed.

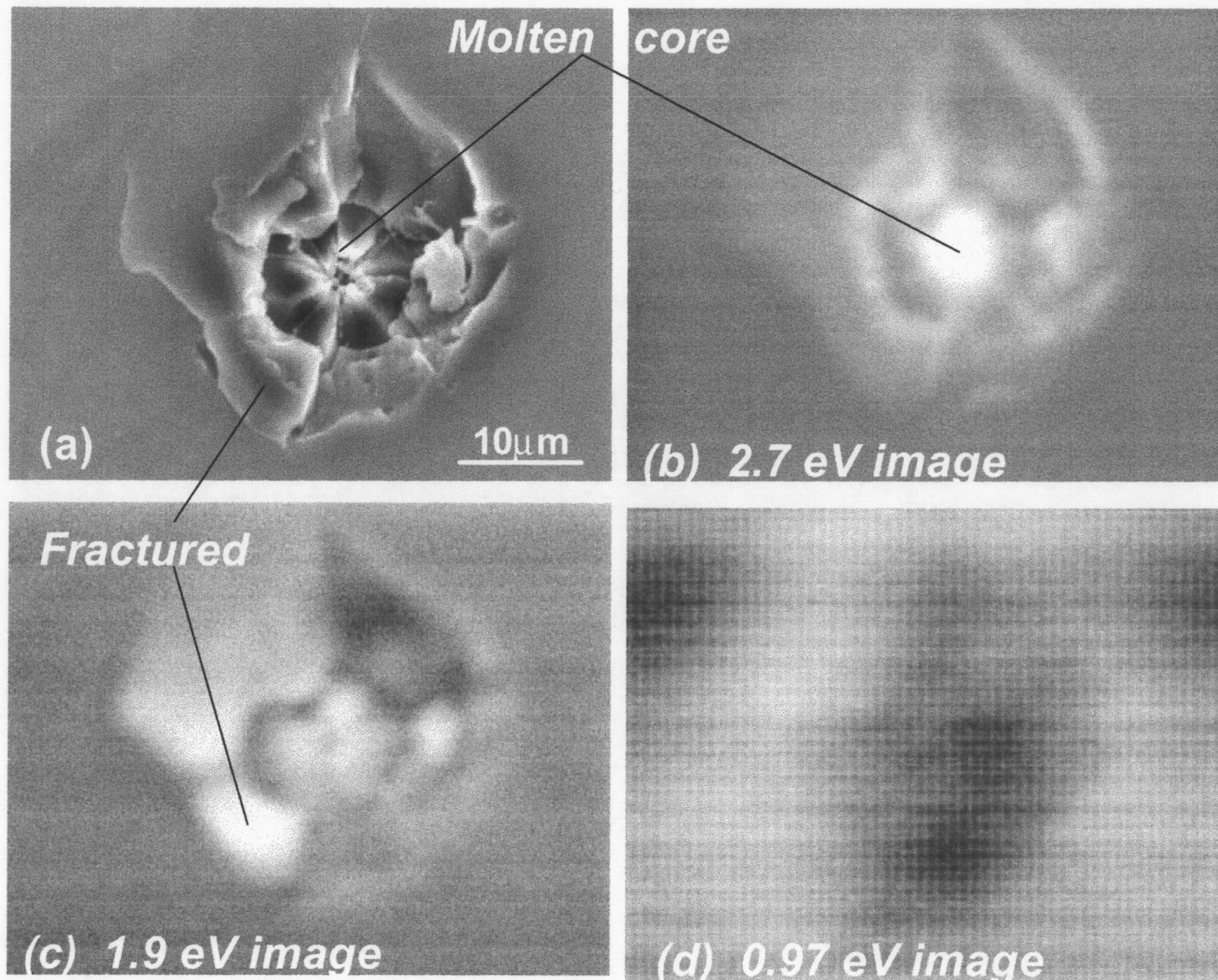


Fig. 2. (a) Secondary electron image, (b) 2.7 eV, (c) 1.9 eV and (d) 0.97eV monochromatic CL images from a damage crater on the exit surface of fused silica induced by one pulse of 3ω light at 45Jcm^{-2} .

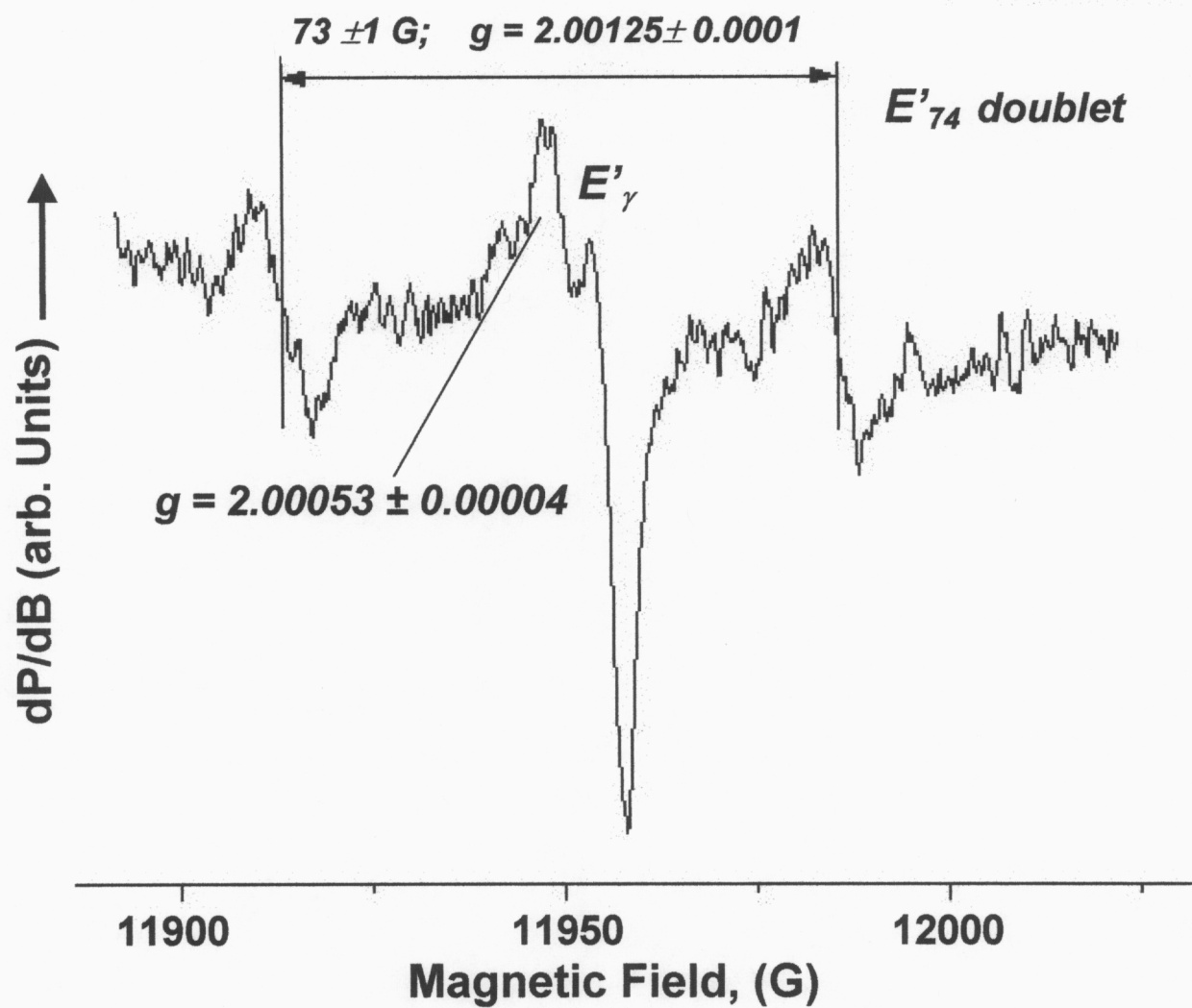


Fig. 3. Q-Band ESR spectrum of 3ω damaged fused silica recorded at 10K. The signal is from ten 1-mm thick disks, each with a damage site initiated with a shot of 3ω light at 30 Jcm^{-2} .